Kevin Murray: Chemistry & Biochemistry
Mentor: Robert Szilagyi -- Chemistry & Biochemistry
Electronic Structure Determination of [Fe]-hydrogenase model complexes

Hydrogenases are a class of metalloenzymes that catalyze the reversible oxidation of dihydrogen to protons. The mononuclear [Fe]-hydrogenases form a unique family of hydrogenase enyzmes in that they function as hydrogen forming methylene-tetrahydromethanopterin dehydrogenases (Hmd). They catalyze the reversible reduction of N5,N10-methyltetrahydromethanopterin with H2 to N5,N10-methylenetetrahydromethanopterin and a proton. In order to understand the electronic structure of the active site of this enzyme, which features a single low-spin iron center, we have studied a series of [Fe]-hydrogenase model complexes provided by a collaborator from Switzerland. X-ray absorption spectroscopy (XAS) data were taken at the S K- and Fe L-edges in order to investigate the electronic structure of these compounds. The studies complexes allowed for a comparative analysis that provided us with how distinct structural elements of the complexes determine overall electronic structure. We utilize calibrated Density Functional Theory-based (DFT) calculations to aid the interpretation of our spectroscopic results. The XAS results allow us to determine the total S 3p and Fe 3d character of the unoccupied frontier orbitals and calculations will allow us to complete the orbital composition so that the total electronic structure is defined.